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Precision Cleaning of Semiconductor Surfaces Using Carbon Dioxide-Based Fluids

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Biography

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Ahmed A. Busnaina, Ph.D., is a Professor and Director of the Microcontamination Research Laboratory, at Clarkson University. He specializes in wafer cleaning technology, chemical and particulate contamination in LPCVD and

sputtering processes, particle adhesion and removal, submicron particle transport, deposition and removal in clean environments. He authored more than 200 papers in journals, proceedings and conferences.

Abstract:

The Los Alamos National Laboratory, on behalf of the Hewlett-Packard Company, is conducting tests of a closed-loop CO₂-based supercritical fluid process, known as Supercritical CO₂ Resist Remover (SCORR). We have shown that this treatment process is effective in removing hard-baked, ion-implanted photoresists, and appears to be fully compatible with metallization systems. We are now performing experiments on production wafers to assess not only photoresist removal, but also residual surface

contamination due to particulates and trace metals.

Dense-phase (liquid or supercritical) CO_2 , since it is non-polar, *acts like* an organic solvent and therefore has an inherently high solubility for organic compounds such as oils and greases. Also, dense CO_2 has a low-viscosity and a low dielectric constant. Finally, CO_2 in the liquid and supercritical fluid states can solubilize metal complexing agents and surfactants. This combination of properties has interesting implications for the removal not only of organic films, but also trace metals and inorganic particulates. In this paper we discuss the possibility of using CO_2 as a precision-cleaning solvent, with particular emphasis on semiconductor surfaces.

Data:

Aqueous-based solutions currently used for wafer cleaning generate large waste streams, and the inherently high surface tension of these solutions limits their use in cleaning substrates containing very-fine-scale structures. Surfactants can be used to reduce surface tension, but this necessitates a subsequent rinsing and drying step, requiring additional amounts of ultrapure water. Also, the withdrawal of wafers through the liquid/gas boundary following the clean invariably leads to re-deposition of particulates.

One of the processes being evaluated for advanced IC manufacturing is dry (vapor-phase) cleaning, to replace traditional aqueous-based immersion cleaning.[1] As an extension of current work on photoresist stripping, performed at Los Alamos on behalf of the Hewlett-Packard Company, we are investigating the possibility of using carbon dioxide (CO_2), either as a liquid or a supercritical fluid, as a precision cleaning solvent.

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. The normal boiling point of liquid water, at one atmosphere, is 100°C . In an open container, Figure 1, the temperature of liquid water cannot be raised above 100°C since this would cause the vapor pressure of the water to rise above one atmosphere,

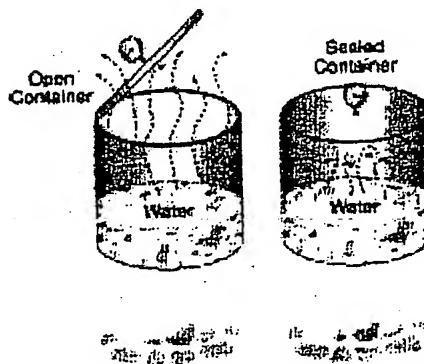


Figure 1. Formation of a supercritical fluid by heating of a liquid in a sealed container.

exceeding the ambient pressure. If we place a quantity of water in a sealed container, however, then we may heat the liquid water to higher temperatures, since the vapor pressure of the water can increase beyond one atmosphere. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until, eventually, the density of the liquid becomes so reduced, and the density of the vapor phase is so increased, that the two densities become equal. The temperature at which the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is

everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical pressure. A fluid which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid. This physical description of the critical temperature and pressure suggests that all simple liquids (and gases) can be made into a supercritical fluid by generating the appropriate conditions of temperature and pressure. This is indeed correct, and Table 1 gives the critical temperature and pressure of some common fluids.

Supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee and essential oils and spices from plants for use in perfumes and foods. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. Table 2 gives a comparison of the diffusivity, viscosity and density of a typical organic fluid in the liquid, gas, and supercritical fluid state.

To a first approximation, the solvent power of a fluid is related to its density. The high, liquid-like densities achievable in supercritical fluids therefore allows for substantial solubilities. Figure 2 shows the pressure-temperature-density surface for pure CO₂. The critical point for pure CO₂, $T_c = 31^\circ\text{C}$ and $P_c = 1072 \text{ psi}$ (≈ 73 atmospheres), is

Table 1. Critical temperature, T_c , and pressure, P_c , for some common fluids.

Fluid	T_c ($^\circ\text{C}$)	P_c (psi)
Neon, Ne	-229	400
Nitrogen, N ₂	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
carbon dioxide, CO ₂	31	1072
sulfur hexafluoride, SF ₆	246	545
propane, C ₃ H ₈	97	617
ammonia, NH ₃	133	1654
water, H ₂ O	374	3209

Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity (cm ² /s)	Viscosity (cP) or (mN·s/m ²)	Density (kg/m ³)
Liquid	10 ⁻⁵	1	1000
Supercritical fluid	10 ⁻³	10 ⁻²	300
Gas	10 ⁻¹	10 ⁻²	1

shown in Figure 2 by the large solid circle. It can be seen that relatively small changes in temperature or pressure, near the critical point, result in large changes in density. It is this tunability of density, and therefore tunability of solvent power, which is one of the most attractive attributes of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity provides for effective penetration into very fine scale structures such as high aspect ratio vias and through holes. Finally, the absence of surface tension provides for excellent wettability.

There has been considerable progress in developing supercritical fluids, and supercritical CO₂ (SCCO₂) in particular, for the precision-cleaning of inorganic surfaces,[2,3,4] including metals,[5,6,7,8] glass,[9,10] optical elements,[11] and one report on its applicability to Si wafers.[12]

One advantage of CO₂ for precision cleaning is that the process leaves no residues, since it evaporates completely when

depressurized. As a result, subsequent aqueous rinsing and drying steps are not required. There is a commercial system available for SCCO₂ cleaning of micro-electromechanical device fabrication,[13] and is becoming a popular processing technique.[14,15,16,17].

Another advantage of CO₂ is its inertness with respect to inorganic materials. Aluminum, which is exposed to dry CO₂, has shown low rates of adsorption and little or no chemical reaction.[18] Pure, dry supercritical CO₂ has been shown to have no

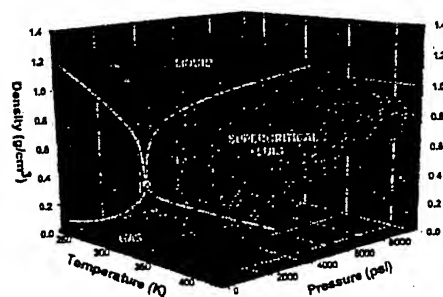


Figure 2. Pressure-temperature-density surface of pure CO₂.

corrosive action on stainless steel,[19] iron,[20] or copper.[21,22,23] It is known from geochemical studies that there is a vanishingly small solubility for SiO_2 in CO_2 . [24,25] Also, Khemka and Chow [26] found that an oxidation anneal of Si in pure CO_2 at 1000 and 1100°C produced an oxide thickness of only 10 nm, independent of annealing time. A thermodynamic analysis of possible reactions between CO_2 and Si_3N_4 [27] shows that, at the temperatures and pressures of semiconductor processing, no reaction between these compounds is expected.

Finally, it has been shown that surface-adsorbed CO_2 does not dissociate for chemically etching with a highly active hydroxylated SiO_2 surface [28].

In this paper, we examine the potential of liquid and supercritical fluid CO_2 for removing organic films, trace metals and particulates from Si wafers. We accomplish this by comparing how immersion in liquid and supercritical CO_2 would behave, relative to immersion in pure water.

1. Organic surface films

SCCO_2 is an excellent solvent for nonpolar, low molecular-

weight organic compounds, such as greases, oils, lubricants and fingerprints.[29,30] It is this ability to solubilize organic compounds which underlies the commercial applications mentioned previously.

Commercial applications for the solubility of organics in liquid CO_2 can be found in [31] while commercial applications for supercritical CO_2 can be found in [32].

2. Trace Metals

Current aqueous immersion cleaning removes metallic contaminants by the formation of soluble metal complexes.

For example, $\text{HCl}/\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions are effective at removing Cu by forming soluble chlorides and sulfates complexes, respectively [33].

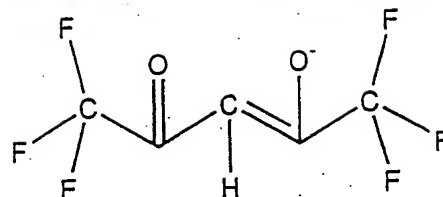
In a similar manner, a reactive component, dissolved in a supercritical fluid, can be used to remove trace metal contaminants either by surface etching of Si and SiO_2 , or by selective chelation. The potential advantage of using SCCO_2 to "scavenge" these metals is an enhanced removal rate resulting from the low viscosity and high diffusivity.

By definition, compounds which are gaseous at the conditions of temperature and pressure of SCCO_2 will be soluble. Therefore,

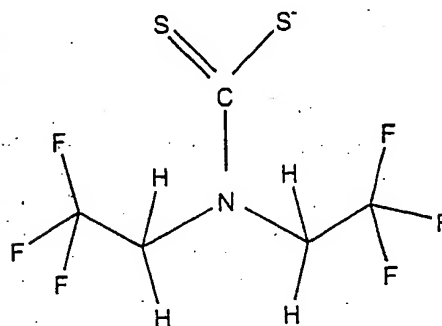
compounds such as SF_6 , Br_2 , and I_2 , which are gases at SCCO_2 conditions, will be soluble in SCCO_2 .

For the case of liquids and solids, the situation is only slightly more complex. While it is well known that CO_2 is capable of solubilizing low molecular weight organic compounds, it is also true that CO_2 can solubilize inorganic compounds, particularly organic compounds, in terms of (a) low molecular weight, (b) nonpolarity, and (c) existing as discrete molecular species. For example, TiCl_4 [34] and SnCl_4 [35,36] have been shown to be very soluble in supercritical CO_2 .

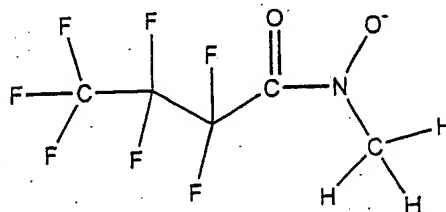
As an example of a potential application, Sugino *et al.* [37] used a dry $\text{Cl}_2 + \text{SiCl}_4$ mixture to remove Fe contamination from Si and SiO_2 surfaces. Both of these compounds are soluble in dense CO_2 . George *et al.* [38] has shown that a very effective compound called 1,1,1,3,3,3-hexafluoro-2,2,2-trifluoroethyl-2,2,2-trifluoroethylthiocarbamate is dissolved in a flowing N_2 stream. This compound, dissolved in a flowing N_2 stream, is used to remove Fe from SiO_2 and Si surfaces. Also, Pearson *et al.* [40] used a compound, dissolved in N_2 , to



a) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione.



b) bis(trifluoroethylthiocarbamate).



c) n-methylheptafluorobutyrylhydroxamic acid.

Figure 3. Structures of some chelating compounds used for chelation/extraction of metals in supercritical CO_2 .

organophosphates.[63,64,65]

3.1. Mechanics of Particle Removal

There are a number of adhesion forces that can act between a particle and a surface, including chemical bonding. In this discussion, however, we will neglect such

Figure 4 shows the types of long-range attractive forces between a particle and a surface. We will assume that the particle is non-magnetic. In addition to the forces shown in Figure 4, we will also consider the magnitude of the gravitational force holding the particle onto the (horizontal) substrate and the capillary forces which exist in humid environments.

There are several components to the van der Waals force between a particle and a surface. The first is a component due to (a) interaction between permanent dipoles (van der Waals-Keesom force), (b) (c) interaction between permanent dipoles and induced dipoles (van der Waals-Debye force), and (d) interaction between induced

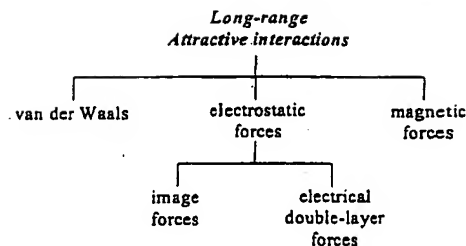


Figure 4. Long-range attractive forces acting between a particle and a surface.[66]

which therefore exhibit only the van der Waals-London force, relates A_{ij} to the work of cohesion:

$$A_{ii} = 24 \pi \gamma_i (d_0^2)_i \quad (7)$$

where γ_i is the surface tension and $(d_0^2)_i$ is approximately equal to the molecular diameter of material i . Using $\gamma_{\text{liquid CO}_2} = 0.6 \text{ dyne/cm}$ at 25°C , [77] and assuming $d_0 = 0.20 \text{ nm}$, [78]

$$A_{33} = A_{\text{liquid CO}_2} = 0.011 \text{ (eV)} \quad (8)$$

This approach cannot be used to calculate the Hamaker constant of SCCO_2 since, by definition, a supercritical fluid has no surface tension. The general expression for the Hamaker constant between molecules of material i is

$$A_{ii} = \pi^2 q^2 \beta_{ii} \quad (9)$$

where q is the number of atoms per unit volume (Loschmidt number), β_{ii} is given by [79]

$$\beta_{ii} = \left(\frac{3}{4} \alpha_0^2 h \nu_0 \right), \quad (10)$$

h is Planck's constant ($h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), ν_0 is the ground-state frequency of the electron

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{e^2}{\alpha_0 m_e}}, \quad (11)$$

e is the electron charge ($e = 1.60 \times 10^{-19} \text{ C}$), m_e is the electron rest mass ($m_e = 9.11 \times 10^{-31} \text{ kg}$), and α_0 is the molecular polarizability. For non-polar molecules like CO_2 , the polarizability can be found from the Clausius-Mossotti (C-M) function

$$\text{C-M} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N_0 \alpha_0 \quad (12)$$

Where ϵ is the dielectric constant, ρ is the density, M is the molecular weight and N_0 is Avogadro's number. Michels and Kleerekoper [80] have shown, through measurements of ϵ and ρ , that over a wide range of temperatures and pressures, including both liquid and supercritical CO_2 , $\alpha_0 = (2.97 - 3.05) \times 10^{-30} \text{ m}^3$

Assuming $\alpha_0 = 3.0 \times 10^{-30} \text{ m}^3$, along with $\rho_{\text{SCCO}_2} = 0.668 \text{ g/cm}^3$ at 50°C and 2000 psi (136 atmospheres), we have $\nu_0 = 1.46 \times 10^{15} \text{ s}^{-1}$,

$\beta_{11} = 8.71 \times 10^{-76} \text{ J}\cdot\text{m}^6$, and

$$A_{33} = A_{\text{SCCO}_2} = 0.045 \text{ (eV)} \quad (13)$$

For comparison, London [81] reports $\alpha_0 = 2.86 \times 10^{-30} \text{ m}^3$ and

$\beta_{11} = 2.18 \times 10^{-77} \text{ J} \cdot \text{m}^6$ for
gaseous CO_2 .

For SiO_2 , Si and water, the following Hamaker constants have been reported: $A_{\text{SiO}_2} = 1.02 \text{ (eV)}$, [82]
 $A_{\text{Si}} = 1.6 \text{ (eV)}$, [83] and
 $A_{\text{H}_2\text{O}} = 0.27 \text{ (eV)}$. [84] Substituting these values into Eq. (6), we have
 $A_{132} = A_{\text{SiO}_2/\text{liq. CO}_2/\text{Si}} = 1.05 \text{ (eV)}$,
 $A_{132} = A_{\text{SiO}_2/\text{SCCO}_2/\text{Si}} = 0.84 \text{ (eV)}$, and
 $A_{132} = A_{\text{SiO}_2/\text{H}_2\text{O}/\text{Si}} = 0.37 \text{ (eV)}$ For comparison, Menon *et al.* [85] gives
 $A_{\text{glass}/\text{H}_2\text{O}/\text{Si}} = 0.07 \text{ (eV)}$. Finally, Eq. (1) gives

$F_{\text{vdW}}^{\text{SiO}_2/\text{liq-CO}_2/\text{Si}} \text{ (dynes)} = 8.762 \times 10^{-3} d$
 $F_{\text{vdW}}^{\text{SiO}_2/\text{SCCO}_2/\text{Si}} \text{ (dynes)} = 7.010 \times 10^{-3} d$
and
 $F_{\text{vdW}}^{\text{SiO}_2/\text{H}_2\text{O}/\text{Si}} \text{ (dynes)} = 3.088 \times 10^{-3} d$,
where d is in microns.

From Eq. (6), it can be seen that the Hamaker constant of the immersed, particle/fluid/surface system is lower than that of the unimmersed particle/substrate system, resulting in a decrease in the van der Waals-London force, due primarily to electrical screening. The reduction is greatest for immersion in water.

B. Electrostatic Force

1. Electrostatic image force

When a charged, insulating particle such as SiO_2 approaches an uncharged conductive surface such as (doped) Si, the requirement for overall charge neutrality generates an equal but oppositely charged "particle" within the Si, Figure 5. These oppositely charged "particles" act, essentially, as two plates of a capacitor, creating a net attractive force. This electrostatic image force, F_{image} , is often the predominate force for larger particles (greater than approximately 5 microns in diameter) [86] and is given by

$$F_{\text{image}} = \frac{Q^2}{4\pi\epsilon_0\epsilon l^2} \quad (14)$$

where Q is the charge on the particle, ϵ is the permittivity of the immersion

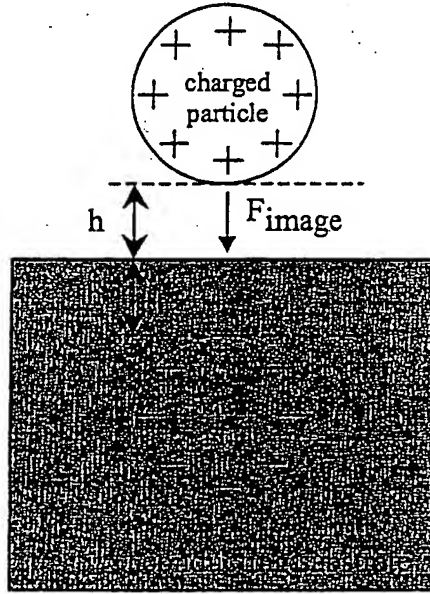


Figure 5. Image force generated by Coulomb attraction between a positively charged particle and its negatively charged "image" particle.

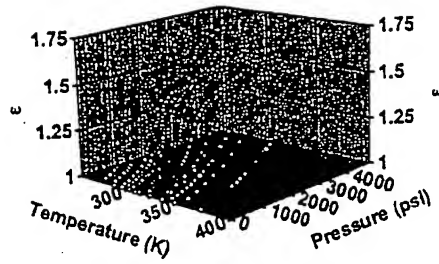


Figure 6. Experimentally measured values of the dielectric constant, ϵ , of pure CO_2 as a function of temperature and pressure.

medium between the particle and the surface, ϵ_0 is the permittivity of vacuum,

$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/(\text{N}\cdot\text{m}^2)$, and l is the separation distance between the charge centers (approximately equal to $2r$ when the charge is uniformly distributed on the particle surface). If the charge density on the SiO_2 particle is 10 electron charges per square micron,[87]

$$F_{\text{image}} (\text{dynes}) = \frac{2.28 \times 10^{-8} d^2}{\epsilon} \quad (15)$$

where d is in microns.

Immersion of the particle/surface system in a fluid affects the magnitude of F_{image} through shielding of electrical charges, as manifested through the dielectric constant. The high static dielectric constant of water, $\epsilon \approx 80$, compared to $\epsilon \approx 1.5$ for liquid CO_2 (15°C and 800 psi), and $\epsilon \approx 1.4$ for SCCO_2 (50°C and

2000 psi) (see Figure 6) results in higher image forces for immersion in CO_2 for a given particle charge.

2. Electrical double layer force

When two dissimilar materials come into contact, a surface contact potential is created due to the difference in their respective work functions. The resulting surface charge buildup needed to preserve charge neutrality sets up a double-layer charge region, creating an electrostatic attraction. In dry environments, this electrical double layer force dominates for smaller particles, less than approximately 5 microns in diameter.[88] This electric double layer force, F_{dbl} , is given by

$$F_{\text{dbl}} = \frac{\pi \epsilon_0 d \phi^2}{2 h} \quad (16)$$

where ϕ is the contact potential established on contact of the two materials and is equal to the numerical difference in their work functions.[89] Assuming $\phi = 0.5 \text{ V}$ [90,91,92,93,94] and again using $h = 4 \text{ \AA}$,

$$F_{\text{dbl}} (\text{dynes}) = 8.69 \times 10^{-4} d \quad (17)$$

where d is in microns.

Immersion in a fluid will affect the magnitude of F_{dbl} layer through charge neutralization.[95] In practice, the initial contact potential will decrease with time because the high electrical conductivity of doped

Si will result in the charge "leaking away".

C. Capillary Force

If a surface-adhered particle is subjected an environment where there is a high vapor pressure of condensable fluid, the fluid may condense in the gaps between the particle and the substrate surface, Figure 7. The surface tension of this condensate draws the surfaces together, resulting in capillary attraction.[96] It is observed that the adhesion of particles to surfaces increases with relative humidity,[97] indicating that capillary force, F_{cap} , can make a significant contribution to overall adhesion. For high relative humidities (> 50 %), for materials which are wetted by the fluid, and for materials having similar wetting properties, F_{cap} is given by [98,99]

$$F_{cap} = 2 \pi d \gamma \quad (18)$$

or

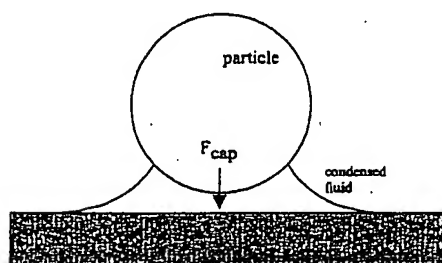


Figure 7. Schematic illustration of the meniscus formed by a condensable fluid and resulting capillary force.

$$F_{cap} \text{ (dynes)} = 6.28 \times 10^{-4} d \gamma \quad (19)$$

where d is in microns and γ is in dynes/cm.

If the particle/substrate system is totally immersed in a fluid which wets both materials, including liquid CO_2 and water, the capillary force should be eliminated.[100] This is also true for SCCO_2 because a supercritical fluid, by definition, cannot be made to condense.

D. Gravitational Force

A solid particle will experience a downward gravitational force, F_{grav} , tending to hold it down onto a horizontal surface. (We assume that the particle is at its distance of closest approach to the substrate so that the buoyancy force can be neglected.) F_{grav} is given by

$$F_{grav} = \frac{\pi}{6} d^3 \rho g \quad (20)$$

For SiO_2 , $\rho = 2.60 \text{ g/cm}^3$ and $g = 980.67 \text{ cm/s}^2$, so that

$$F_{grav} \text{ (dynes)} = 1.34 \times 10^{-9} d^3 \quad (21)$$

where d is in microns.

If the particle and the substrate surface are immersed, then the actual particle density, ρ , should be replaced by the apparent density, $(\rho - \rho_{fluid})$. However, the densities of liquid CO_2 , supercritical CO_2 and

water are similar, Figure 2, so that Eq. (21) will not be greatly changed.

Thus far, we have considered "static" forces acting between the SiO₂ particle and the Si surface. Typically, however, particulate removal is accomplished by immersion cleaning with a *flowing* solvent. This fluid motion generates two additional, hydrodynamic forces: lift and drag. In the following sections, the magnitudes of these forces will again be examined for liquid CO₂, supercritical CO₂ and liquid water as the immersion media, for both laminar and turbulent flow conditions.

E. Drag Force

O'Neill [101] gives an exact solution to the linearized Stokes flow equation for the case of a uniform linear shear flow, Figure 8, and for low values of the Reynolds number

$$F_{\text{drag}} = 1.7009 \times 3 \pi \eta d V_{y=r} \quad (22)$$

where $V_{y=r}$ is the fluid velocity at a distance r normal to the substrate surface (r is the radius of the particle). For laminar flow, the velocity gradient is related to the fluid viscosity by

$$\tau_0 / \eta = \left(dV/dy \right)_{y=0} \quad (23)$$

where τ_0 is the shear stress on the substrate surface due to the flow.[102] Also, since the velocity gradient of the flow is linear, we can integrate Eq. (23) from $y = 0$ to $y = r$, where $V = 0$ at $y = 0$:

$$r \tau_0 = \eta V_{y=r} \quad (24)$$

Substituting into Eq. (22), and collecting terms,

$$F_{\text{drag}} = 8.02 d^2 \tau_0 \quad (25)$$

Chitanvis *et al.*[103] have carried out an analysis for the case of turbulent flow with a viscous sublayer, deriving an expression for the drag force as a function of the fluid (stream) velocity, V :

$$F_{\text{drag}} = 10.2 \pi \rho \left(\frac{f}{2} \right) V^2 r^2 \quad (26)$$

where f is Fanning's friction factor, $f = 0.04$. Simplifying Eq. (26) gives

$$F_{\text{drag}} = 0.16 \rho V^2 d^2 \quad (27)$$

Comparing this drag force with the frictional force, which varies linearly with particle diameter, they further show that the removal of the smallest particles by rolling varies as $V^{-4/3}$ while removal by sliding varies as V^{-2} .

F. Lift Force

The (idealized) gradient in flow velocity illustrated in Figure 8 shows that the flow past a surface-adhered particle is a function of the distance normal to the surface. The lower flow velocity at the bottom of the particle relative to the velocity of flow at the top of the particle results in a lifting force, tending to dislodge the particle in the direction of the surface normal. This force is exactly analogous to the lift generated by airfoils. The magnitude of the lift force, F_{lift} , will depend on the nature of the near-surface flow, and expressions have been put forward for different flow conditions.

Saffman [104] gives the inertial lifting force in a linear shear flow as

$$F_{\text{lift}} = 6.46 r^2 \eta^{-1/2} \left(\frac{dv}{dy} \right)^{1/2} V_{y=r} \quad (28)$$

where $v = \eta/\rho$. This equation was derived for the case of a small spherical particle in an unbounded, linear shear flow in the absence of wall effects, but serves as an approximation to the problem of a particle in a shear flow along a rigid wall.[105] As before,

$$\left(\frac{dv}{dy} \right)_{y=0} = \frac{\tau_0}{\eta} \quad (29)$$

and

$$r \tau_0 = \eta V_{y=r} \quad (30)$$

Combining Eqs. (28-30) gives [106]

$$F_{\text{lift}} = 1.615 \eta^{-1} \rho^{1/2} \tau_0^{3/2} d^3 \quad (31)$$

In turbulent flow, where the turbulent flow component normal to the substrate surface varies quadratically with distance from the surface, Cleaver and Yates [107] give the lift force as

$$F_{\text{lift}} = 0.076 \rho \left(\frac{\eta}{\rho} \right)^2 \left(\frac{d \rho U^*}{\eta} \right)^3 \quad (32)$$

Again using Eqs. (29) and (30), we have

$$F_{\text{lift}} = 0.076 \eta^{-1} \rho^{3/2} \tau_0 d^3 \quad (33)$$

3.2. Surfactants

Surfactants, in addition to lowering the surface tension of liquids, are used to assist in particle removal by modifying the surface

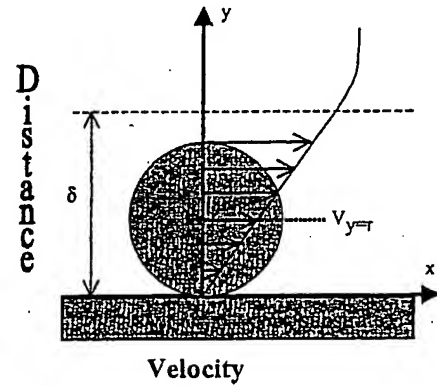
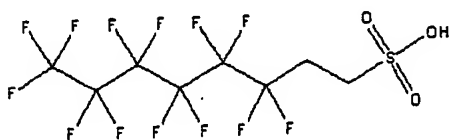


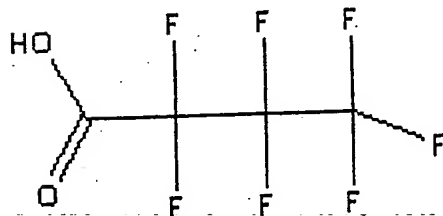
Figure 8. Schematic illustration of a linear shear flow past a surface-adhered particle.

charge/zeta potential of particle and/or substrate surfaces.[108] There are several compilations on the solubility of commercial surfactants in liquid and supercritical CO₂. [109,110,111] These

compilations show that there are anionic, cationic and nonionic surfactants which have significant solubilities. Also, considerable progress has been made in the design of surfactants specifically for use in supercritical CO₂, where it is well-known that highly fluorinated compounds exhibit excellent solubilities.[112,113] Figure 9 shows



1H,1H,2H,2H-
Perfluorooctanesulfonic acid,
miscible at P = 144 bar and
T = 50°C [114].



perfluorobutyric acid, miscible at
P = 186 bar and T = 50°C [115]

Figure 9. Examples of surfactants which are completely miscible in supercritical CO₂, along with the conditions where complete miscibility is observed.

two representative examples of perfluorinated surfactants and the conditions of temperature and pressure where complete solubility in supercritical CO₂ is observed.

3. Discussion

The ability of CO₂, particularly in the supercritical state, to remove organic contaminants would seem superior to the use of aqueous systems, which normally contain oxidizers along with acids or alkalies, since the former would be much less corrosive to fabricated surface structures.

The removal of trace metals using a sequence of acidic and/or alkaline aqueous rinses, i.e., SC-1 and SC-2, is capable of producing low levels of trace metals. Pure CO₂ does not solubilize these metals due to charge neutrality considerations, and would require the use of chelators. However, there are many such compounds which have been shown to be soluble and these would be required in very small amounts. Although any additive is undesirable in terms of potential residues, a final rinse using clean, dry CO₂ should remove these.

Inspection of Table 3 shows that, in general, adhesion forces between a particle and a surface vary linearly with the particle diameter. Removal forces, however, vary as a higher power of d (hydrodynamic drag acts on the cross-sectional area of the particle and therefore scale as

d^2 , while hydrodynamic lift, vibrational and centrifugal forces act on the volume of the particle and therefore scale as d^3). Consequently, particle removal becomes more difficult as the particle size decreases.[116]

The calculations of the Hamaker constant for liquid and supercritical CO₂ presented here are only approximate, but it is apparent that the resulting values of the van der Waals-London forces are higher than the corresponding value for immersion in water.

For the image force, it can be seen that the lower dielectric constant of both liquid and supercritical CO₂ results in larger values of the image force, for a given particle charge.

Exact calculations for the lift and drag forces on a surface-adhered particle are extremely complex, and allow only trends to be deduced. However, the lift force depends inversely on fluid viscosity, which favors CO₂, Figure 10. For the drag force a higher viscosity is preferred, which is not favorable for CO₂. However, the boundary layer thickness, which is proportional to $\sqrt{\eta/\rho}$, would be much thinner. Also, the addition of soluble polymers might be used to independently adjust the viscosity of liquid and/or

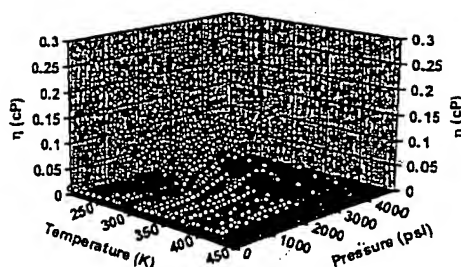


Figure 10. Empirically measured viscosity, η , in centipoise (cP) of pure CO₂, as a function of temperature and pressure.

supercritical CO₂.

It has been mentioned that the migration of surface-adhered particles due to Brownian motion and their subsequent agglomeration may be a mechanism by which the smallest particles are removed. This motion is greatly enhanced in both liquid and supercritical CO₂ because of the low viscosity. The mean-square displacement, \bar{x} , by Brownian motion is given by

$$\bar{x} = \sqrt{\frac{2 k T t}{3 \pi \eta d}} \quad (34)$$

where T is the absolute temperature and t is time. The lower viscosity of liquid and supercritical CO₂ (approximately a factor of 50 compared to water), along with the van der Waals attractive forces which exist between particles, would promote this agglomeration.[117]

Table 3. Effect on the various adhesion forces between a SiO_2 particle contacting a flat, horizontal Si surface immersed in (a) liquid CO_2 , and (b) supercritical CO_2 (SCCO₂), and (c) H_2O , based on the empirical relationships for these forces. All forces are given in dynes.

	$\text{SiO}_2/\text{liq. CO}_2$ /Si	$\text{SiO}_2/\text{SCCO}_2$ /Si	$\text{SiO}_2/\text{water}$ /Si
F_{vdW}	$8.76 \times 10^{-3} d$	$7.01 \times 10^{-3} d$	$3.09 \times 10^{-3} d$
F_{dbl}	$8.69 \times 10^{-4} d$	$8.69 \times 10^{-4} d$	$8.69 \times 10^{-4} d$
F_{image}	$1.52 \times 10^{-8} d^2$	$1.62 \times 10^{-8} d^2$	$2.85 \times 10^{-10} d^2$
F_{cap}			$(6.28 \times 10^{-4} d \gamma)$
F_{drag}	$8.02 d^2 \tau_0$	$8.02 d^2 \tau_0$	(laminar flow) $8.02 d^2 \tau_0$
	ρ similar \therefore similar F_{drag}	ρ similar \therefore similar F_{drag}	(turbulent flow) $0.16 \rho V^2 d^2$
F_{lift}	lower $\eta \rightarrow$ ρ similar \therefore higher F_{lift}	lower $\eta \rightarrow$ ρ similar \therefore higher F_{lift}	(laminar flow) $1.615 \eta^{-1} \rho^{1/2} \tau_0^{3/2} d^3$
	lower $\eta \rightarrow$ ρ similar \therefore higher F_{lift}	lower $\eta \rightarrow$ ρ similar \therefore higher F_{lift}	(turbulent flow) $0.076 \eta^{-1} \rho^{3/2} \tau_0 d^3$
F_{grav}	similar F_{grav}	similar F_{grav}	$1.34 \times 10^{-9} d^3$

Based on the foregoing analysis of adhesion forces for immersion in CO_2 versus water, it is probable that additional removal forces must be generated if dense-phase CO_2 is to achieve comparable removal forces obtainable with water-immersion. These forces can be generated in a number of ways, including increased shear flow, either through higher volumetric

flow rates or mechanical agitation of the wafer, or electrical forces.

We are currently performing experiments on pre-contaminated wafers to quantitatively evaluate the ability of dense-phase (liquid and supercritical) CO_2 to remove particulates, and the results of this study will be the subject of a future report.

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